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Influence of silicon doping on vacancies and optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films

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Influence of silicon doping on vacancies and optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films

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The authors have used positron annihilation spectroscopy and photoluminescence measurements to study the influence of silicon doping on vacancy formation in AlGaInSi structures. The results show a correlation between the Doppler broadening measurements and the intensity from 510 nm photoluminescence transition. The reduction in the W parameter when the $[\text{Si}]/[\text{Al}+\text{Ga}]$ fraction in the gas phase is above 3×10^{-4} indicates that the positrons annihilate in an environment where less Ga $3d$ electrons are present, i.e., they are trapped in group-III vacancies. The observation of vacancies at these silicon concentrations coincides with the onset of the photoluminescence transition at 510 nm. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721132]

UV devices based on AlGaIn alloys have gained a lot of interest in recent years and are already commercially available.¹ AlGaIn systems are especially suitable for these applications since they cover wavelengths from 200 to 364 nm. For almost any semiconductor system, one of the crucial requirements is the possibility to produce and control the doping of the layers. Previously, n -type doping of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ was considered a problem since the carrier concentration decreased with increasing Al mole fraction x .² Progress in this field has been made by several groups and low resistivity $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers as well as n -type doping of AlN have been reported.^{3–6}

Silicon is the most commonly used element of n -type doping of AlGaIn structures. Hence, the reason for its electrical deactivation with increasing Al mole fraction has been the focus of some debate lately. Calculations by Van de Walle *et al.* showed that the Al vacancy can act as a compensator in its triply ionized state, with the Fermi level close to the conduction band in AlN .⁷ Furthermore, since the band gap increases with increasing Al content, the formation energy for the group-III vacancy decreases. Wagener *et al.* reported on the deepening of the Si level with increasing Al content ($x=0.2$ – 0.5), as well as on the presence of two levels in the band gap thought to be responsible for the compensation.⁸ Keller *et al.* proposed that observed PL transition in the 510–550 nm range is due to the group-III vacancy.⁹

In this letter, we confirm the correlation between the vacancy concentration in the group-III sublattice and the photoluminescence (PL) transition in the 510–550 nm range by combining positron annihilation spectroscopy (PAS) with photoluminescence measurements. Furthermore, we have investigated the effect of silicon doping concentration on vacancy formation in AlGaIn layers. We observe an increase both in the PL intensity and the vacancy concentration when

the $[\text{Si}]/[\text{Al}+\text{Ga}]$ fraction in the gas phase increases above 3×10^{-4} .

For these experiments, $\text{Al}_{0.63}\text{Ga}_{0.37}\text{N}:\text{Si}$ films of different doping levels were grown by metal-organic chemical vapor deposition. The aluminum and gallium sources were TMAI and TMGa, and the nitrogen source NH_3 . The substrates used were $4H$ -SiC, upon which buffer layers of 150 nm of AlN followed by 460 nm of unintentionally doped $\text{Al}_{0.63}\text{Ga}_{0.37}\text{N}$ were deposited. The doped layers in question were 300 nm thick, with a dislocation density of $5 \times 10^9 \text{ cm}^{-2}$. The $[\text{Si}]/[\text{Al}+\text{Ga}]$ ratio was varied from 3.5×10^{-5} to 6×10^{-4} over the five samples by modifying the Si_2H_6 precursor flow. The dislocation density did not depend on the $[\text{Si}]/[\text{Al}+\text{Ga}]$ ratio.

Hall measurements performed on the samples at room temperature showed a linear increase in carrier concentration with increasing Si content up to a $[\text{Si}]/[\text{Al}+\text{Ga}]$ ratio of 3×10^{-4} , while the mobility decreased linearly over the same sample range. Above this level of Si content, the carrier concentration decreased slightly while the mobility decreased at a sharper rate of decline. Further details on the electrical characteristics have been published in Ref. 10.

In order to determine the vacancy content in the thin layers, we used a variable energy positron beam. After implantation the positrons thermalize rapidly and diffuse in the lattice until they annihilate with electrons. Neutral and negative vacancy-type defects in the lattice act as positron traps. When a positron is trapped by a vacancy, the positron-electron momentum distribution narrows and the momentum of the annihilating positron-electron pair can be detected as a reduction in Doppler broadening of the 511 keV annihilation line. For the description of shape of the broadened annihilation line, we used the conventional S and W parameters.¹¹ The S parameter is the fraction of annihilation events in the central part of the annihilation peak and thus describes annihilation mainly with low momentum valence electrons. The W parameter is calculated from the wings of the annihilation peak and describes annihilation mainly with high momentum core electrons. Generally an increase (decrease) in the $S(W)$ parameter indicates the presence of vacancy-type defects. In

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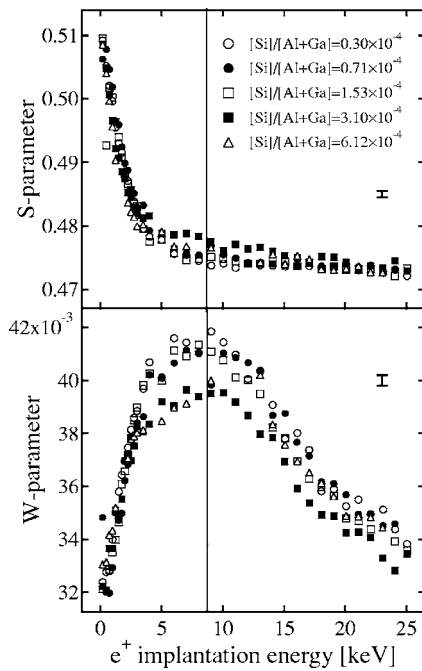


FIG. 1. Valence annihilation parameter S and high momentum annihilation parameter W as a function of positron implantation energy for the investigated samples. The vertical line in the figure indicates where the mean positron implantation depth coincides with the interface between the AlGaIn:Si and AlGaIn. Also indicated in the figure is the typical error of the parameters.

this study the parameter energy windows were chosen as $|E_{\gamma}-511 \text{ keV}| < 0.83 \text{ keV}$ and $3.00 \text{ keV} < |E_{\gamma}-511 \text{ keV}| < 7.60 \text{ keV}$ for the S and W parameters, respectively.

Photoluminescence measurements were performed on all samples at room temperature using a pulsed ArF excimer laser at a wavelength of 193 nm as an excitation source. The laser repetition rate was 20 Hz with a pulse duration of 9 ns and an average power density of 100 mW/cm^2 focused to a minimum spot size of $100 \mu\text{m}$. Photoluminescence spectra were collected using a 0.55 m focal length spectrometer ($f/6.4$) with a UV-enhanced charge-coupled device detector. The data were not corrected for the detector response function.

Figure 1 shows the PAS Doppler broadening parameters S and W as a function of positron implantation energy. Indicated in the figure with a vertical line is the positron implantation energy at which the positron mean implantation depth coincides with the interface between the AlGaIn:Si and the unintentionally doped AlGaIn. At low implantation energies $E < 3 \text{ keV}$ the measured S and W parameters in all of the studied samples are approximately equal, as is expected when the positron annihilation is dominated by diffusion of the implanted positrons to the sample surface. In the energy interval of 3–10 keV a clear peak is seen in the W parameter. Above 10 keV the W parameter starts to decrease toward the SiC substrate value. The S parameter shows less features and the samples with different Si contents are more difficult to distinguish. However, the samples with the two highest Si concentrations have a slightly higher S parameter in the AlGaIn:Si layer.

As can be seen from the W parameter in Fig. 1, the samples are divided into two groups when comparing the W parameters in the peak region, where the annihilation signal mainly comes from the silicon doped layer. The differences

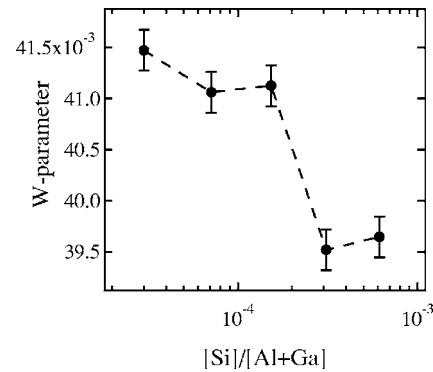


FIG. 2. High momentum annihilation parameter W in the AlGaIn:Si layers as a function of Si fraction in the layers.

between the samples can be easily observed in Fig. 2, where the W parameter in the AlGaIn:Si layer is presented as a function of the $[\text{Si}]/[\text{Al}+\text{Ga}]$ fraction in the gas phase. A change in the W parameter to lower values can be seen when the silicon fraction reaches 3×10^{-4} indicating that the annihilation environment of the positrons changes. This fraction corresponds to a free electron concentration of $7.5 \times 10^{18} \text{ cm}^{-3}$.

The main contributors to the momentum intensity in the W parameter region are Ga $3d$ electrons. Thus, the reduction in the W parameter when the silicon doping in AlGaIn reaches approximately 3×10^{-4} is due to a reduction in the Ga content in the environment of the annihilating electron positron pair. This means that the positron is trapped by a defect surrounded by nitrogen atoms, i.e., a group-III vacancy. An estimate for the vacancy concentration can be obtained when assuming that the W parameter for the group-III vacancy in AlGaIn is similar to that in GaN.¹² The deduced vacancy concentration in the samples with the silicon fraction of 3×10^{-4} or higher is thus in the 10^{17} – 10^{18} cm^{-3} range.

The PL spectra of the AlGaIn:Si films were characterized by bright band edge related luminescence at 254 nm. Two characteristic deep level transitions were also observed in all samples, one centered at 410 nm and a second one at 510 nm. A detailed investigation of the impact of the growth conditions on the PL properties previously performed⁹ in the same reactor and combined with secondary-ion-mass spectroscopy analysis indicated that the relative intensity of the 410 nm level increased with the impurity concentration in the films, in particular, oxygen. In contrast, the 510 nm level did not show any correlation with the residual impurities in the films and was tentatively associated with a native defect, the group-III vacancy, in Ref. 9. The relative PL intensity between this transition and the band edge emission as a function of Si content is shown in the inset of Fig. 3.

The comparison between the trends observed in PL and in the positron annihilation experiments, showing a direct correlation between the luminescence peak centered around 510 nm and the W parameter confirms its association with the group-III vacancy or a complex involving the group-III vacancy. Since the 410 nm level follows the same trend with increasing Si doping, this level is probably also associated with a vacancy in the group-III sublattice. A likely candidate for a group-III vacancy complex is $V_{\text{Ga}}-\text{O}_{\text{N}}$, which is typical in GaN (Refs. 12–14) and has also been predicted theoretically.⁷

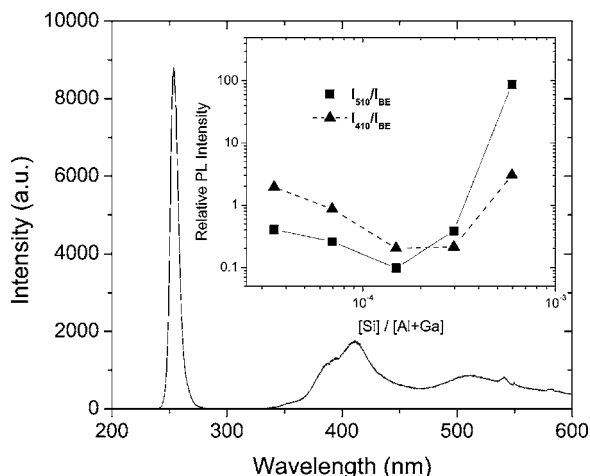


FIG. 3. PL spectra of an AlGaIn:Si film with a $[\text{Si}]/[\text{Al}+\text{Ga}]$ ratio of 1.5×10^{-4} . Inset: relative PL intensity as a function of the Si fraction in the layer.

We have combined positron annihilation spectroscopy and photoluminescence measurements to study the influence of silicon doping on vacancy formation in AlGaIn:Si layers. A clear correlation is found between silicon concentration, PAS Doppler parameters S and W , and observed defect transitions in the PL measurements. We conclude that the vacancies in the group-III sublattice are responsible for the observed PL transitions at 510 nm. The vacancies appear when the $[\text{Si}]/[\text{Al}+\text{Ga}]$ ratio in the gas phase is above 3×10^{-4} .

- ¹E. Monroy, F. Omn  s, and F. Calle, *Semicond. Sci. Technol.* **18**, R33 (2003).
- ²A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, G. G. Milviskii, J. M. Redwing, M. Shin, M. Skowronski, D. W. Greve, and R. G. Wilson, *Solid-State Electron.* **42**, 627 (1998).
- ³Y. Taniyasua, M. Kasu, and N. Kobayashi, *Appl. Phys. Lett.* **81**, 1255 (2002).
- ⁴M. L. Nakarmi, K. H. Kim, K. Zhu, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* **85**, 3769 (2004).
- ⁵Y. Taniyasua, M. Kasu, and T. Makimoto, *Appl. Phys. Lett.* **85**, 4672 (2004).
- ⁶P. Cantu, S. Keller, U. K. Mishra, and S. P. DenBaars, *Appl. Phys. Lett.* **82**, 3683 (2003).
- ⁷C. G. Van de Walle, C. Stampfl, J. Neugebauer, M. D. McCluskey, and N. M. Johnson, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G10.4 (1999).
- ⁸M. C. Wagoner, G. R. James, and F. Omn  s, *Appl. Phys. Lett.* **83**, 4193 (2003).
- ⁹S. Keller, P. Cantu, C. Moe, Y. Wu, Sa. Keller, U. K. Mishra, J. S. Speck, and S. P. DenBaars, *Jpn. J. Appl. Phys., Part 1* **44**, 7227 (2005).
- ¹⁰C. G. Moe, H. Masui, M. C. Schmidt, L. Shen, B. Moran, S. Newman, K. Vampola, T. Mates, S. Keller, J. S. Speck, S. P. DenBaars, C. Hussel, and D. Emerson, *Jpn. J. Appl. Phys., Part 2* **44**, L502 (2005).
- ¹¹K. Saarinen, P. Hautoj  rvi, and C. Corbel, in *Identification of Defects in Semiconductors*, Semiconductors and Semimetals, edited by M. Stavola (Academic, New York, 1998), 51A, p. 209.
- ¹²S. Hautakangas, I. Makkonen, V. Ranki, M. J. Puska, K. Saarinen, X. Xu, and D. C. Look, *Appl. Phys. Lett.* **86**, 031915 (2005).
- ¹³J. Oila, J. Kivioja, V. Ranki, K. Saarinen, D. C. Look, R. J. Molnar, S. S. Park, S. K. Lee, and J. Y. Han, *Appl. Phys. Lett.* **82**, 3433 (2003).
- ¹⁴F. Tuomisto, K. Saarinen, B. Lucznik, I. Grzegory, H. Teisseyre, T. Suski, S. Porowski, P. R. Hageman, and J. Likonen, *Appl. Phys. Lett.* **86**, 031915 (2005).